

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
16 August 2001 (16.08.2001)

PCT

(10) International Publication Number  
**WO 01/59825 A1**

- (51) International Patent Classification<sup>7</sup>: **H01L 21/311**, **VAN BAEKEL**, Kristel; 4050 Lakeside Drive, Richmond, CA 94806 (US)  
G03F 7/42
- (21) International Application Number: PCT/US01/04348
- (22) International Filing Date: 8 February 2001 (08.02.2001)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:  
60/181.131 8 February 2000 (08.02.2000) US
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- (81) Designated States (*national*): JP, KR.
- (84) Designated States (*regional*): European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR).
- Published:**  
— with international search report  
— before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

*For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*



**WO 01/59825 A1**

(54) Title: METHOD FOR REMOVING PHOTORESIST AND RESIDUES FROM SEMICONDUCTOR DEVICE SURFACES

(57) Abstract: The present invention is a novel process for removing photoresist, post-etch polymers, and other assorted residues from semiconductor devices incorporating low- $\kappa$  dielectric materials. In general the invention comprehends using a substantially oxygen free reducing plasma that is preferably high in hydrogen content, rather than the oxidizing plasma typically used. The invention generally comprises the steps of (a) introducing a semiconductor device including a dielectric material comprising an organic silicon glass into a chamber, (b) introducing effective amounts of a hydrogen containing gas such as ammonia or methane, and (c) decomposing the gases and plasma phase reacting the decomposed gases with the photoresist and or other residues to volatilize the residues. In one preferred embodiment of the method the etchant gasses include ammonia, helium, and a forming gas preferably comprising hydrogen and nitrogen. In a second preferred embodiment, the etchant gasses include ammonia and a forming gas comprising hydrogen and helium. In a third preferred embodiment, the forming gas is replaced with water vapor preferably created in a catalytic moisture generator by combining hydrogen in a helium carrier gas, with oxygen.

## METHOD FOR REMOVING PHOTORESIST AND RESIDUES FROM SEMICONDUCTOR DEVICE SURFACES

### 5 FIELD OF THE INVENTION

This invention relates generally to ammonia based methods for stripping photoresist and post-etch polymers during integrated circuit manufacturing processes, and more particularly to processes for removing photoresist and post-etch polymers or  
10 residues from the surface of integrated circuit devices with a combination of gasses, including ammonia.

### BACKGROUND OF THE INVENTION

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Conventional fabrication of an integrated circuit device involves placing numerous device structures, such as MOSFETs, bipolar transistors, and doped contact regions, on a single monolithic substrate. The device structures are then electrically interconnected with horizontal conductive lines or structures formed in layers and  
20 vertical conductive structures called vias between layers so as to implement desired circuit function.

In order to produce ever faster and smaller integrated circuit devices, the integrated circuit industry has continuously increased the density of the device  
25 structures on the substrate surface. The increasingly higher device structure density has resulted in a continuous reduction in the separation between conductive structures and layers of materials, a reduction in the width and thickness of conductive lines and an increase the total length of the conductive lines. This has further resulted in a number of adverse effects. For example, by reducing the spacing between conductive  
30 materials in the integrated circuit device, an increase in a phenomenon known as parasitic capacitance or capacitive crosstalk is observed, wherein a change in voltage on one conductive structure effect the voltage on nearby conductive structures. As the

conductive structures of an integrated circuit are packed more closely together this capacitance between the conductive structures increases. One solution is to reduce the capacitance by using insulating or dielectric materials having a lower dielectric value ( $\kappa$ ) than the widely used silicon oxides.

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A variety of such low- $\kappa$  materials are currently under consideration and development. These new dielectrics can be organic or inorganic in composition, and are typically deposited using chemical vapor deposition (CVD) methods, or by spin-on glass (SOG) techniques. One challenge encountered in using the new materials relates to the photoresist stripping and post-etch polymer removal steps used in current manufacturing processes. Generally, current known photoresist stripping and polymer removal methods, particularly those using  $O_2$ , have adverse effects on the low- $\kappa$  materials. Specifically, the oxygen can attack the bonds between the atoms in inorganic low- $\kappa$  materials such as Si-H and Si-C oxidizing them to Si-O and SiOH respectively. The presence of Si-O and Si-OH may adversely effect the  $\kappa$  value of the material. When using organic low- $\kappa$  materials, the  $O_2$  plasma may oxidize the carbon low- $\kappa$  material much as it does the photoresist forming volatile CO and  $CO_2$ , thus removing low- $\kappa$  material that was intended to remain.

What is needed are methods for photoresist stripping and post-etch polymer removal that avoid the disadvantages of the prior art.

## SUMMARY OF THE INVENTION

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Accordingly, the present invention is a novel process for removing photoresist (sometimes referred to as "resist"), post-etch polymers and other assorted residues (sometimes referred to hereafter as "polymer," "sidewall polymer," "via veil," or "residue") from semiconductor devices incorporating low- $\kappa$  dielectric materials. This process may be useable on a variety of organic and inorganic low- $\kappa$  materials, however, this specification will emphasize its use on organo-silica glass - type (OSG) low- $\kappa$  materials.

The novel method of the present invention comprehends using a reducing plasma that is preferably high in hydrogen content and substantially oxygen free, rather than the oxidizing plasma typically used. A hydrogen containing gas such as Ammonia or Methane is used as the primary source of hydrogen radicals that remove the photoresist and post strip residues by chemical reduction instead of chemical oxidation. Ammonia has been found to be particularly effective in removing photoresist and post strip residues from materials that are sensitive to the standard chemistry using oxygen.

10

In general, the invention is a method for removing photoresist and other residues comprises the steps of (a) introducing a semiconductor device into a chamber including a dielectric material comprising an organo-silica glass, (b) introducing effective amounts of a hydrogen containing etchant gas such as ammonia and or methane to remove a layer of photoresist and or other residues, (c) decomposing the etchant gasses and plasma phase reacting the decomposed gases with the photoresist and or other residues to volatilize the residues.

15

In one preferred embodiment of the method the etchant gasses include ammonia, helium, and a forming gas preferably comprising approximately 5% hydrogen and 95% nitrogen. In a second preferred embodiment, the etchant gasses include ammonia and a forming gas comprising approximately 4% hydrogen and approximately 96% helium. In a third preferred embodiment, the forming gas is replaced with water vapor preferably created in a catalytic moisture generator.

20

Three example methods of the invention will be discussed including (1) organo-silica glass photoresist stripping using an ammonia based plasma with  $H_2/N_2$  forming gas, (2) organo-silica glass photoresist stripping using an ammonia based plasma with  $H_2/He$  forming gas, and (3) organo-silica glass photoresist stripping using an ammonia based plasma with  $H_2O$  process gas substituted for the forming gas of prior listed methods.

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## BRIEF DESCRIPTION OF THE DRAWINGS

- 5           FIG. 1    is a cutaway side view of a semiconductor device, prior to  
                  conductive lines being formed in the first metal layer, with a metal  
                  layer disposed over underlying layers, a low-k dielectric layer  
                  disposed over the metal layer, and a layer of photoresist disposed  
                  over the low- $\kappa$  dielectric layer with apertures formed in the  
                  photoresist to define areas where the dielectric will be etched.
- 10           FIG. 2    is a cutaway side view of the semiconductor device of FIG. 1 after  
                  the low-k dielectric has been etched.
- 15           FIG. 3    is a cutaway side view of the semiconductor device of FIG. 2 after  
                  the method of the invention has been applied to remove the  
                  photoresist layer and any sidewall polymers or residues.

## DETAILED DESCRIPTION OF THE INVENTION

20           Accordingly, the present invention is a novel process for removing photoresist,  
                  post-etch polymers, and other assorted residues from semiconductor devices  
                  incorporating low- $\kappa$  dielectric materials. This process may be useable on a variety of  
                  organic and inorganic low- $\kappa$  materials, however, this disclosure will emphasize its use  
25           on organo-silica glass – type low- $\kappa$  materials. In general, the invention comprehends  
                  using a reducing plasma that is preferably high in hydrogen content and substantially  
                  oxygen free to prevent oxidation of the low- $\kappa$  material, rather than the oxidizing  
                  plasma typically used.

30           The term “substantially oxygen free” is used in this application to mean that  
                  the quantity of oxygen molecules in the reaction chamber is low enough that the  
                  oxygen does not significantly influence or affect the results. There is one exception to

the above definition relating to embodiments of the method including the addition of water vapor, wherein the term "substantially oxygen free" means that the oxygen level in the reaction chamber is low enough that there is no appreciable or unacceptable oxidation damage to the low-  $\kappa$  dielectric material portion of the semiconductor devices being treated therein.

The methods of the invention may be implemented with any suitable plasma stripping or etching system. In the methods described, reactive species derived from etchant gases are generated in a plasma, and these species diffuse to the photoresist and/or post-etch polymers and/or residues where the reactive species chemically react to produce desired chemical changes in the nature of the photoresist or residues. Typically the reaction removes the photoresist and residues by creating volatile by-products that are de-sorbed from the surface of the semiconductor device. However, the desired reaction could instead result in a residue that is prepared for removal in a subsequent process step.

The method of the invention may be implemented with any suitable plasma stripping or etching system, and is not limited to the particular configurations that may be disclosed herein. The assembly of such systems is well known, and many such assemblies exist in a variety of configurations. The exact configuration of the system may be varied as required, and the details of the particular system used will depend on the parameters of the process that must be controlled, and the specific application of the system. However, microwave plasma systems are currently preferred for use with the method of the invention. Plasma stripping and etching systems generally comprise a number of interconnected components including (a) an etching chamber that can be evacuated to reduce the gas pressures therein, (b) a pumping system for establishing and maintaining the desired pressure, (c) various pressure gauges to monitor the pressure in the chamber, (d) apparatus allowing the pressure in the chamber and the flow rate of gasses into the chamber to be controlled independently, (e) a power supply, (f) gas handling apparatus for metering and controlling the flow of reactant gases, and (g) one or more means for creating a plasma and for maintaining the plasma.

In general, one or more process gasses are introduced into the chamber from one or more gas sources through an inlet pipe. A microwave source, preferably at the inlet pipe, causes a microwave plasma to be formed at the inlet pipe, thus discharging  
5 a reactive gas with a high concentration of free radicals. The gas passes through openings in a top electrode mounted above a wafer, where additional energy may be applied to the plasma. Under appropriate conditions, the reactive gas can decompose and remove unwanted residues and photoresist by converting the photoresist and residues to volatile gases. A vacuum draws the gasses away through an exhaust tube,  
10 and also maintains the pressure in the chamber within a desired range. Such processes are well known in the prior art for processing currently used dielectric materials such as SiO<sub>2</sub>. However, current known photoresist stripping and polymer removal methods, particularly those using O<sub>2</sub>, have adverse effects on new lower- $\kappa$  dielectric materials.

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The novel method of the present invention comprehends using a reducing plasma that is preferably high in hydrogen content and oxygen free to prevent oxidation, rather than the oxidizing plasma typically used. A hydrogen containing gas such as Ammonia or Methane is used as the primary source of hydrogen radicals that  
20 remove the photoresist and post strip residues by chemical reduction instead of chemical oxidation. Ammonia has been found to be particularly effective in removing photoresist and post strip residues from materials that are sensitive to the standard chemistry using oxygen.

25 In general, the invention is a method for removing photoresist and other residues comprising the steps of (a) introducing a semiconductor device into a chamber, preferably but not necessarily including a dielectric material comprising an organic silicon glass, (b) introducing effective amounts of hydrogen containing etchant gas such as ammonia or methane, (c) decomposing the gasses and plasma  
30 phase reacting the decomposed gases with the photoresist and/or other residues to treat or volatilize the residues. The method is preferably performed in a substantially oxygen free environment. Other gasses, in addition to ammonia, may be introduced

during step (c) including but not limited to nitrogen, helium, hydrogen, and water vapor. The method of the invention may be used with many known integrated circuit manufacturing processes including, but not limited to, current conventional fabrication processes, damascene processes, and copper damascene processes.

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FIGS. 1 through 3 illustrate one application or example of use of the method of the invention in a process for forming via holes in a layer of dielectric material deposited over a metal layer in which conductive lines have been formed. FIG. 1, shows a semiconductor device 100 on which known methods are used to form  
10 conductive lines in a metal layer 102 disposed over the underlying layers 104. The metal layer 102 typically actually comprises several layers of different metals or alloys including barrier layers, seed layers, etc. A dielectric layer 106 is then formed over the metal layer 102. Any desired dielectric material may be used, and the particular dielectric material used is not critical to the invention, although the use of a  
15 low-k dielectric material is preferred. The method of applying the dielectric layer 106 is also not critical to the invention, and examples of acceptable methods for depositing the dielectric layer 106 include known chemical vapor deposition methods, physical vapor deposition methods, and spin-on deposition methods. Then, using known methods, the dielectric layer 106 is planarized, and coated with a photoresist mask.  
20 The dielectric layer 106 typically comprises a number of layers which may include several types of dielectrics, and silicon oxide and or silicon nitride caps or barriers.

Conventional spin-on methods are preferred for forming the photoresist layer 108, however, other methods of applying the photoresist 108 may be acceptable. To  
25 enhance the photo-lithographic process, anti-reflective coatings may be deposited prior to the photoresist 108. The photoresist 108 is cured in a conventional manner that depends on the particular photoresist material chosen. Typically, the photoresist 108 is exposed through a mask to an agent such as UV light, electron beam, or X-rays. Then, the photoresist 108 is developed to produce regions or gaps 110 where  
30 the photoresist 108 has been removed to allow etching materials access to the underlying dielectric layer 106, as is seen in FIG. 1



Referring to FIG. 2, the dielectric layer 106 underlying the photoresist layer 108 is etched through the gaps 110. This results in the formation of via holes 112 to receive conductive material that will form vias. The particular etching method is not critical to the invention. Typically, certain residues remain after etching, including sidewall polymers, or via veils 114, as shown. Generally there is some over etching to insure that quality vias have been formed, and this results in inorganic material being incorporated into the via veils 114.

Application of the methods of the invention results in the semiconductor device 100 of FIG. 3, which shows the photoresist 108 and the via veils 114 removed. Although a conventional via etching process has been shown, the method of the invention may be used in many other semiconductor manufacturing processes.

As previously stated, the method steps of the invention comprises the steps of (a) introducing a semiconductor device into a chamber including a dielectric material, preferably a low-k dielectric material, (b) introducing effective amounts of hydrogen containing etchant gas such as ammonia or methane, (c) decomposing the gasses and plasma phase reacting the decomposed gasses with the photoresist and/or other residues to treat or volatilize the residues. Other gasses, in addition to ammonia, may be introduced during step (c) including but not limited to, helium, hydrogen, water vapor, and forming gas.

In one preferred embodiment of the method the etchant gasses include ammonia, helium, and a forming gas preferably comprising approximately 5% hydrogen and 95% nitrogen. In a second preferred embodiment, the etchant gasses include ammonia and a forming gas comprising approximately 4% hydrogen and approximately 96% helium. In a third preferred embodiment, the forming gas is replaced with water vapor preferably created in a catalytic moisture generator by combining approximately 4% hydrogen and approximately 96% helium, with oxygen.

The forming gas, as defined herein, is a gas mixture that contains hydrogen in an inert (non-flammable) gas, such as argon, helium, or nitrogen. Forming gas allows

the use of hydrogen as a process gas, but with a reduced flammable hazard. The forming gas can be made in any desired percentage hydrogen content, however, a hydrogen content of 5% or less is preferred.

5       The word "inert" when applied to components of the forming gas refers only to the gases flammability. Even though the "inert" portion of the forming gas is inert when considered for flammability, or reaction within the CMG, it may not necessarily be inert when reacting with the wafer in the plasma chamber. As the inert portion of the gas passes downstream, it too is part of the plasma in the reactor chamber, and the  
10       results of the method can be affected by the "inert" portion.

The methods described above will be disclosed in more detail below by way of example. These processes may include several steps, or sub-steps, the order of which may vary from one situation to another.

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#### EXAMPLE 1.

The first example discloses a method using an ammonia-based plasma with an  $H_2/N_2$  Forming Gas. The preferred process variables used in this example are as  
20       follows:

- (1) The reaction chamber gas pressure is preferably between 200 and 2100 mtorr, and more preferably approximately 500 to 800 mtorr.
- (2) The Microwave power level is preferably between 800 and 4,400 watts,  
25       and more preferably approximately 2700 watts.
- (3) The platen temperature is preferably 15 to 250 degrees centigrade, and more preferably approximately 250 degrees centigrade.
- (4) The ammonia gas flow is preferably between 200 and 5,500 sccm, and more preferably approximately 1360 sccm.
- 30       (5) The helium flow is preferably between 0 and 1,500 sccm, and more preferably approximately 1360 sccm.

- (6) The forming gas flow is preferably between 0 and 5,500 sccm, and more preferably approximately 4080 sccm. Furthermore, the forming gas preferably comprises approximately 5% Hydrogen and 95% Nitrogen.
- (7) The RF power level is preferably between 0 and 600 watts.

5

The experiment was performed on organo-silicate glass substrate samples. The results were evaluated by scanning electron microscope, and the surface of the oxide hard mask on the organic silicon glass substrate appeared clear of all residue and photoresist and the via hole appears intact and free from sidewall residues. The results on blanket coated samples were evaluated with the use of an ellipsometer to determine the thickness and refractive index. The refractive index is used to screen for a change in the physical properties of the low- $\kappa$  dielectric material. The analysis of the data from the ellipsometer showed negligible degradation of the refractive index of the material, with the observed degradation on the order of less than one percent.

15

## EXAMPLE 2.

The second embodiment of the method of the invention comprises an ammonia-based plasma with an  $H_2/He$  Forming Gas. The substitution of  $H_2/He$  forming gas for the  $H_2/N_2$  forming gas, as shown in the previous example, appeared to give similar results with a faster photoresist removal rate. The preferred process variables used in this example are as follows:

20

- (1) The reaction chamber gas pressure is preferably between 200 and 2100 mtorr, and more preferably approximately 800 mtorr.
- (2) The Microwave power level is preferably between 800 and 4,400 watts, and more preferably approximately 2700 watts.
- (3) The platen temperature is preferably 15 to 250 degrees centigrade, and more preferably approximately 250 degrees centigrade.

30

- (4) The ammonia gas flow is preferably between 200 and 3,000 sccm, and more preferably approximately 1360 sccm.
- (5) The forming gas flow is preferably between 4,000 and 6,000 sccm, and more preferably approximately 5440 sccm. Furthermore, the forming gas preferably comprises approximately 4% Hydrogen and 96% Helium.
- (6) The RF power level is preferably between 0 and 600 watts.

As before, the results were evaluated by SEM microscope observations, and the surface of the oxide hard mask appeared clear of all residue and photoresist and the via holes appears intact and clear of sidewall residues.

### EXAMPLE 3

The third embodiment of the method of the invention comprises the use of an ammonia-based plasma with  $H_2O$ . The substitution of  $H_2O$  as a process gas for the  $H_2/N_2$  forming gas, as discussed previously, may give similar results. As previously mentioned, the water vapor is preferably produced in a catalytic moisture generator (CMG) by reacting excess  $H_2$  in a He carrier with  $O_2$ . However, this process should be effective with  $H_2O$  being derived from other sources such as heated liquid sources. When using a CMG for this process, it is preferable to run with stoichiometric excess of  $H_2$  so that the  $O_2$  is substantially consumed in the CMG unit and not allowed into the reactor as free  $O_2$ .

When  $H_2$  containing forming gas is used together with oxygen in a catalytic moisture generator to make water vapor, the reaction is exothermic. At flows, near or above 15 liter per minute, the temperature of a typical catalytic moisture generator casing can rise from 100 to 300 C. In addition, the higher the concentration of hydrogen in the forming gas, the hotter the reaction. For reasons of safety, the hydrogen containing forming gas preferably comprises less than 6%  $H_2$ .

In the exemplary method described below, there is an inherent relationship between the amount of water vapor and the amount of inert gas. As one introduces

the forming gas through the CMG, for each hydrogen molecule ( $H_2$ ) entering, there is one water molecule ( $H_2O$ ) formed. And if stoichiometric amounts of oxygen flow are used, then the effluent gas is merely water vapor and the inert gas. For example, if a forming gas that had 4% hydrogen in helium was used (and there was a stoichiometric amount of oxygen), then the effluent from the CMG is 4% water vapor and the remaining 96% is helium. In some embodiments it is preferred that no additional amount of inert gas is introduced into the process stream above and beyond the amount that enters the CMG.

The preferred process variables used in this example are as follows:

- (1) The reaction chamber gas pressure is preferably between 800-1600 mtorr, and more preferably approximately 800 mtorr.
- (2) The Microwave power level is preferably 1,700 to 2,700 watts, and more preferably approximately 2700 watts.
- (3) The platen temperature is preferably 150 to 250 degrees centigrade, and more preferably approximately 250 degrees centigrade.
- (4) The ammonia gas flow is preferably between 1,300 and 4,300 sccm, and more preferably approximately 2,225 sccm.
- (5) The forming gas flow is preferably between 4,000 and 6,000 sccm, and more preferably approximately 5440 sccm. Furthermore, the forming gas preferably comprises approximately 4% Hydrogen and 96% Helium.
- (6) The flow of Oxygen is preferably at a rate approximately stoichiometrically equivalent to the hydrogen flow rate, plus or minus up to 50%.

As before, the results were evaluated by SEM microscope observations, and the surface of the oxide hard mask appeared clear of all residue and photoresist and the via holes appears intact and clear of sidewall residues.

To those skilled in the art, many changes and modifications will be readily apparent from the consideration of the foregoing description of a preferred embodiment without departure from the spirit of the present invention; the scope thereof being more particularly pointed out by the following claims. For example, it is possible to integrate the process steps of the invention in integrated circuit fabrication processes other than those discussed herein. The description herein and the disclosures hereof are by way of illustration only and should not be construed as limiting the scope of the present invention which is more particularly pointed out by the following claims.

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## CLAIMS

What is claimed is:

- 1 1. A method for removing photoresist and for removing organic and inorganic  
2 residues from the surface of a semiconductor device, the method comprising:  
3  
4 (a) placing a semiconductor device, having a residue formed thereon, into  
5 a reaction chamber,  
6  
7 (b) creating and maintaining a substantially oxygen free environment  
8 within the reaction chamber  
9  
10 (c) introducing etchant gasses into the reaction chamber, the etchant  
11 gasses including a hydrogen containing gas selected from the group  
12 consisting of  $\text{CH}_4$  and  $\text{NH}_3$ ,  
13  
14 (d) applying energy to the etchant gasses to generate a plasma,  
15  
16 (e) exposing the semiconductor device to the plasma for a selected period  
17 of time,
- 1 2. The method of claim 1, wherein the etchant gasses include a hydrogen  
2 containing forming gas.
- 1 3 The method of claim 2, wherein the hydrogen containing forming gas includes  
2 a dilutant selected from the group consisting of nitrogen, helium, argon, or nitrogen.
- 1 4. The method of claim 1, wherein water vapor is introduced to the reaction  
2 chamber.

1 5. The method of claim 1 wherein the semiconductor device comprises a low-k  
2 dielectric material.

1 6. The method of claim 5 wherein the low-k dielectric material is an organo-  
2 silicate dielectric material

1 7. A method for removing photoresist and for removing organic and inorganic  
2 residues from the surface of a semiconductor device, the method comprising:

3

4 (a) placing a semiconductor device comprising a low-k dielectric material,  
5 into a reaction chamber, the semiconductor device having a residue  
6 formed thereon,

7

8 (c) creating and maintaining a substantially oxygen free environment  
9 within the reaction chamber

10

11 (b) introducing etchant gasses into the reaction chamber, the etchant  
12 gasses including a hydrogen containing gas,

13

14 (c) applying energy to the etchant gasses to generate a plasma,

15

16 (d) exposing the semiconductor device to the plasma for a selected period  
17 of time,

1 8. The method of claim 7, wherein the hydrogen containing gas comprises at  
2 least one gas selected from the group consisting of  $\text{CH}_4$  and  $\text{NH}_3$ .

1 9. The method of claim 7, wherein the etchant gasses include a hydrogen  
2 containing forming gas.



1 10. The method of claim 7, wherein the hydrogen containing forming gas includes  
2 a dilutant selected from the group consisting of helium, argon, or nitrogen.

1 11. The method of claim 7, wherein water vapor is introduced to the reaction  
2 chamber.

1 12. A method for removing photoresist and for removing organic and inorganic  
2 residues from the surface of a semiconductor device, the method comprising:

3

4 (a) placing a semiconductor device comprising a low-k dielectric material,  
5 into a reaction chamber, the semiconductor device having a residue  
6 formed thereon,

7

8 (b) creating and maintaining a substantially oxygen free environment  
9 within the reaction chamber

10

11 (c) introducing etchant gasses into the reaction chamber, the etchant  
12 gasses including a hydrogen containing gas selected from the group  
13 consisting of ammonia and methane,

14

15 (d) applying energy to the etchant gasses to generate a plasma,

16

17 (d) exposing the semiconductor device to the plasma for a selected period  
18 of time.

1 13. The method of claim 12, wherein the etchant gasses include a hydrogen  
2 containing forming gas.

1 14. The method of claim 13, wherein the hydrogen containing forming gas  
2 includes a dilutant selected from the group consisting of, helium, argon, or nitrogen.

1 15. The method of claim 12, wherein water vapor is introduced to the reaction  
2 chamber.

1 16. The method of claim 15, wherein water vapor is generated using a catalytic  
2 moisture generator.

1/1

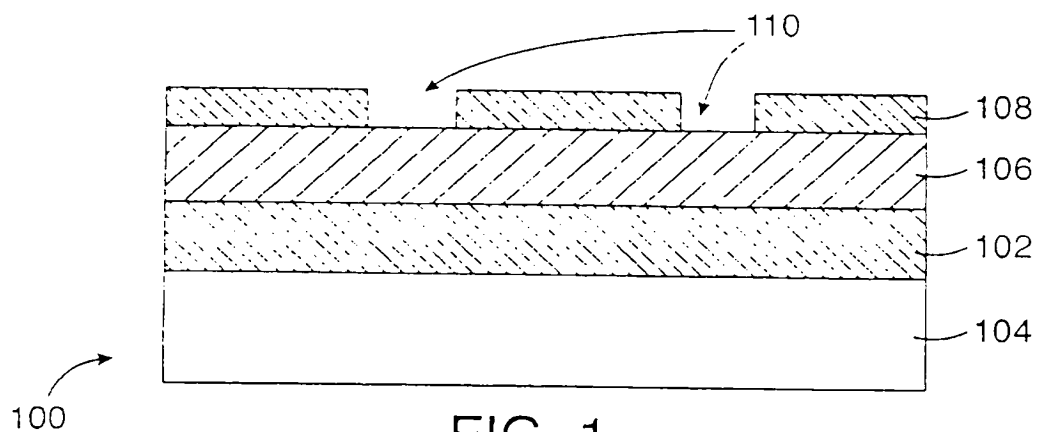


FIG. 1

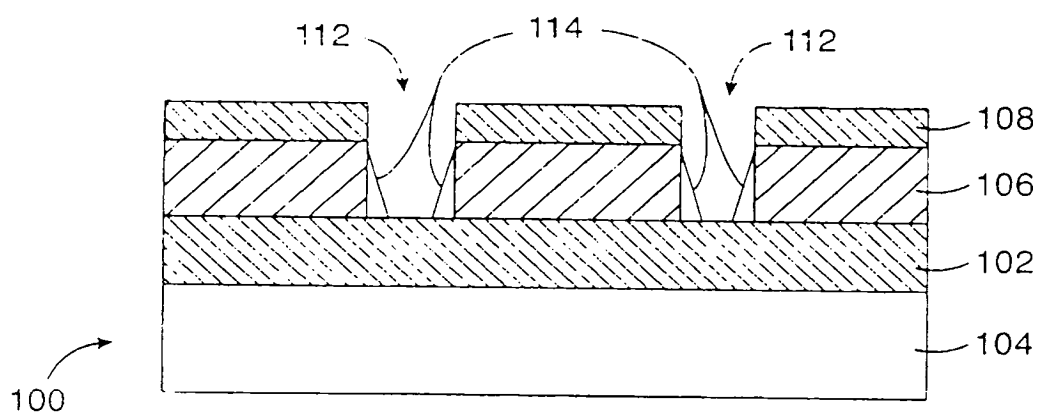


FIG. 2

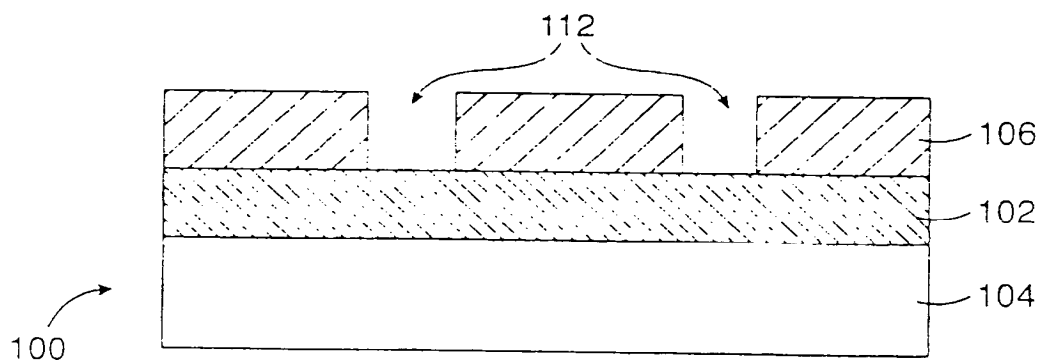


FIG. 3

# INTERNATIONAL SEARCH REPORT

International Application No.

PCT/US 01/04348

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 7 H01L21/311 G03F7/42

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 H01L G03F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

PAJ, WPI Data, EPO-Internal, INSPEC

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 1999, no. 11, 30 September 1999 (1999-09-30) -& JP 11 150101 A (NEC CORP), 2 June 1999 (1999-06-02) abstract	1,5-8,12
A	paragraph '0025! -& US 6 124 213 A (NEC CORPORATION) 26 September 2000 (2000-09-26) the whole document	2,3,9, 10,13,14
X	EP 0 305 946 A (TOKYO SHIBAURA ELECTRIC CO) 8 March 1989 (1989-03-08) column 9 -column 11	1
A		4,7,8, 11,12,15
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

31 May 2001

Date of mailing of the international search report

07/06/2001

Name and mailing address of the ISA

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## INTERNATIONAL SEARCH REPORT

Internat Application No

PCT/US 01/04348

## C. (Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 463 870 A (FUJITSU LTD) 2 January 1992 (1992-01-02)	1
A	column 5, line 29 - line 51; claims 1-3	4,7,8, 11,12,15
X	----- LOUIS D ET AL: "Post etch cleaning of low-k dielectric materials for advanced interconnects: characterization and process optimization" MICROELECTRONIC ENGINEERING, NL, ELSEVIER PUBLISHERS BV., AMSTERDAM, vol. 41-42, 1 March 1998 (1998-03-01), pages 415-418, XP004111746 ISSN: 0167-9317 paragraph '02.3! -----	7

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 01/04348

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP 11150101 A	02-06-1999	US 6124213 A	26-09-2000
EP 0305946 A	08-03-1989	JP 1200628 A	11-08-1989
		JP 1086521 A	31-03-1989
		DE 3855636 D	05-12-1996
		DE 3855636 T	27-03-1997
		US 5298112 A	29-03-1994
		JP 2049425 A	19-02-1990
		JP 2724165 B	09-03-1998
		KR 9207449 B	01-09-1992
EP 0463870 A	02-01-1992	DE 69130909 D	01-04-1999
		DE 69130909 T	24-06-1999
		JP 2038407 C	28-03-1996
		JP 5102092 A	23-04-1993
		JP 7075229 B	09-08-1995
		KR 9405287 B	15-06-1994
		US 5403436 A	04-04-1995

Form PCT/ISA/210 (patent family annex) (July 1992)